applied sciences

MDPI

Article

Comparison of Microencapsulated Phase Change Materials Prepared at Laboratory Containing the Same Core and Different Shell Material

Jessica Giro-Paloma [1,*], Cemil Alkan [2], Josep Maria Chimenos [1] and Ana Inés Fernández [1]

[1] Departament de Ciència de Materials i Química Física, Universitat de Barcelona, C/Martí i Franquès, 1, 08028 Barcelona, Spain; chimenos@ub.edu (J.M.C.); ana_inesfernandez@ub.edu (A.I.F.)

[2] Department of Chemistry, Gaziosmanpaşa University, 60240 Tokat, Turkey; cemil.alkan@gop.edu.tr

* Correspondence: jessicagiro@ub.edu; Tel.: +34-934037244

Academic Editor: Luisa F. Cabeza

Received: 16 June 2017; Accepted: 11 July 2017; Published: 14 July 2017

Abstract: Microencapsulated Phase Change Materials (MPCM) are widely used in active and passive systems for thermal energy storage. To evaluate the strength of a proper shell/PCM system, comparisons were performed between laboratory-prepared MPCM samples produced by in situ polymerization with a phase change temperature of 50 °C and a particle size of around 1–2 μm with tetracosane as PCM, and polystyrene (PS) and poly (methyl methacrylate) (PMMA) as shells. Evaluation of mechanical performance was performed for different samples by means of Atomic Force Microscopy (AFM) at different temperatures (23 °C and 60 °C) and with different encapsulation ratios (1:3 and 1:1, shell:core) in order to compare their properties with the PCM below and above its phase change. Evaluations of the Effective Young's modulus (*E*) and deformation properties were performed for both types of MPCM. For an encapsulation mass ratio of 1:3, PS has better mechanical properties because, when increasing the temperature, the *E* decreases less than with PMMA. In the comparison between PS/tetracosane systems with different encapsulation mass ratios (1:3 and 1:1), *E* values were higher for the 1:3 encapsulation mass ratio at both temperatures under study. This means that, in terms of mechanical and thermal properties, the best combination core/shell/encapsulation mass ratio is PS/tetracosane/1:3.

Keywords: phase change material; microencapsulated phase change material; atomic force microscopy

1. Introduction

Phase Change Materials (PCMs) are a solution widely used for decreasing a building's energy consumption [1] by storing and releasing heat within a certain temperature range, raising the buildings inertia, and stabilizing indoor climates. However, because PCMs cyclically change their phase from solid to liquid during the charging and discharging of the heat storage process, there is a necessity for retaining the PCMs in containers or matrices. The methodologies by which PCM are confined depend on the thermal energy storage (TES) application. Among the available methodologies, the encapsulation of PCM in a container as a supporting material that maintains the shape of the Microencapsulated Phase Change Material (MPCM) when transitions occur has been explored, this being this one of the most efficient ways of confining PCM [2]. There are several advantages for MPCM over PCM, such as providing a large heat transfer area, the reduction of the PCM reactivity towards the outside environment, and the ability to control the variations in volume of the storage materials as phase change occurs [3], among others. In building applications, for example, the organic PCM is encapsulated not only for preventing leakage but for preventing the evaporation or release of some of their components [4].

Although it is important to distinguish between different MPCM usages in passive and active solar systems, the chemical, physical, thermal, and mechanical properties have to be evaluated in the same way. A passive solar system does not involve mechanical devices or conventional energy sources beyond those needed to regulate dampers and other controls. Examples of basic passive solar structures are greenhouses, sunrooms, and solariums. In terms of design, the success of the passive solar system will depend on the orientation and the thermal mass of the structure's exterior walls, as these factors determine their ability to store and redistribute heat. On the other hand, active solar energy systems use the same basic principles as passive systems, except that they use a heat transfer fluid (for example water) to absorb heat. Active solar systems use external sources of energy to pumps and other types of equipment to collect, store and convert solar energy.

Around fifty different polymers, both natural and synthetic, can be employed as shell materials in the microencapsulation process for MPCMs [5]. The polymeric shell has to be capable of creating a thin film, cohesive and stable, coating the PCM. Hence, the polymeric shell has to be chemically compatible and non-reactive with the core material, as well as able to polymerize in an aqueous medium. Furthermore, the strength, flexibility, impermeability, and stability have to be adequate for the whole system. The thickness of the shell can vary depending on the encapsulation methodology. A good option for a polymeric shell is poly (methyl methacrylate) (PMMA), because it has suitable mechanical properties, is an adaptable material, and offers decent protection against the environment [6–8]. It has also been reported elsewhere [9–14] that polystyrene (PS) is also a good option for encapsulating PCM. Regarding PCM, the material that is to be coated will depend on its final application [15–18]. Its composition can be a single solid substance or a combination of active constituents [19–21]. PCM can be organic, inorganic, or eutectic, but a high thermal energy storage capacity is required, and is the most important property to take into account.

Although there are a lot of studies considering commercial samples such as Micronal® DS 5001 [22–31], there have also been MPCMs produced in research laboratories with good results [9,32–34], some of which have been characterized for evaluating their possible usage at industrial scale. Most of the studies that characterize MCPM take into account the chemical, physical, and thermal properties, but few characterize their mechanical properties by Atomic Force Microscopy (AFM) with indentation mode [35]. The relevance of mechanical property evaluation lies in the importance of analyzing the MPCM in service conditions when the PCM is in solid and liquid states [36].

The goal of this paper was to test the mechanical properties (Effective Young's modulus, E and deformation) of two laboratory-made tetracosane MPCMs with nominal diameters of around 1–2 μm, in order to evaluate their stiffness and decide the best shell between PMMA and PS based on their mechanical properties. Additionally, the mechanical response based on differences in the encapsulation ratio between shell and core—1:3 and 1:1—was also evaluated.

2. Materials and Methods

The procedure for manufacturing the MPCM was in situ polymerization [5]. The two kinds of MPCM had different polymeric shells: poly(methyl methacrylate) (PMMA) and polystyrene (PS), respectively. For both types of shell, the core of the PCM was tetracosane, $C_{24}H_{50}$, with a melting temperature of around 50 °C. Moreover, two encapsulation mass ratios (shell:core), 1:3 and 1:1, were tested. The average diameter for all microcapsules was 1–2 μm.

MMA monomer and ethyleneglycol dimethacrylate crosslinker were both obtained from Merck Company (Darmstadt, Germany). They were used after NaOH solution (10 wt % in water) treatment to remove monomethylether hydroquinone inhibitor. Tertbutylhydroperoxide initiator from Merck Company (Darmstadt, Germany) was used as received. Ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) and ammonium persulphate (Sigma-Aldrich company, St. Louis, MO, USA) were also initiators and used as received. Triton X-100 was used as surfactant, and was supplied by Sigma-Aldrich (Darmstadt, Germany).

In this study, mechanical tests were performed using the Atomic Force Microscopy (AFM) technique with a Peak Force Quantitative NanoMechanics mode (QNM) instrument (Terrassa, Spain).

A Multimode 8, Nanoscope V electronics system was used. Additionally, a diamond AFM probe MDNISP with a nominal spring constant of 388 nN·nm^{-1} was also used. The sensitivity was 68.2 nm·V^{-1}, and the set point was between 400 and 550 nN. The peak force amplitude was 150 nm.

Sample preparation consisted of the previous elaboration of slurries by mixing manufactured MPCM with ethanol. Then, 50 µL of slurry was poured on freshly cleaved mica and gently dried with a nitrogen stream. The vertical force required to plastically deform the microcapsules was tested in triplicate for both PMMA:tetracosane and PS:tetracosane samples. Furthermore, topographic images before and after each indentation were taken. These images before and after performing the tests were acquired for each sample at 23 °C and 60 °C to compare the properties of both behaviors when the PCM was in solid state (below its phase change) and liquid state (above to its phase change).

3. Results and Discussion

The Effective Young's modulus (E) at 23 °C and 60 °C was evaluated for three different samples at each temperature on the top of the microcapsules. In Figure 1, the histograms displaying the results for the sample composed of PMMA and tetracosane (1:3) for both temperatures are shown. This is a graphical representation of the data distribution as a probability distribution estimation of a quantitative variable. The difference obtained when increasing the temperature is noticeable. At 23 °C, the E value of the PMMA microcapsules had a mean of 2.7 GPa, while at 60 °C this value dramatically decreased to 0.1 GPa. That is, there was a 96% of E reduction between the temperatures.

The histograms showing the results for PS and tetracosane (1:3) are shown in Figure 2. In this case, E at 23 °C had an average value of 1.5 GPa, while E at 60 °C was 1.1 GPa. This means a 27% reduction of Effective Young's Modulus between the temperatures. Accordingly, and only taking into account the E values, it would be better to use polystyrene (PS) as a shell in a MPCM system due to the E value not decreasing so abruptly when the temperature rises.

Additionally, tests were performed to evaluate the maximum force that can be applied on the top of the microcapsule before breaking it. In the case of the MPCM formed using PMMA as the shell and tetracosane as a PCM, this force at 23 °C was 31.2 µN, as shown in Figure 3. In a typical loading curve, the applied force is proportional to the deflection error, and Z (nm) is the penetration of the tip inside the sample. Four subsections can be taken into account in this kind of graph: (a) No contact between sample and tip. In the graph, this point (a) is marked with an arrow and an image of the sample before applying forces has also been added. This is the first part of the blue continuous line; (b) Plastic deformation or plastic penetration of the sample. There is a change in the slope, which can be defined as the maximum force that can be applied to the sample. This is the area between two vertical discontinuous lines, and is also marked with an arrow; (c) Deformation of the sample; (d) Retraction of the AFM probe until there is no contact between the tip and the sample, which is marked by a red discontinuous line. Most of the time, the end of line (d) and the beginning of line (a) are overlapped.

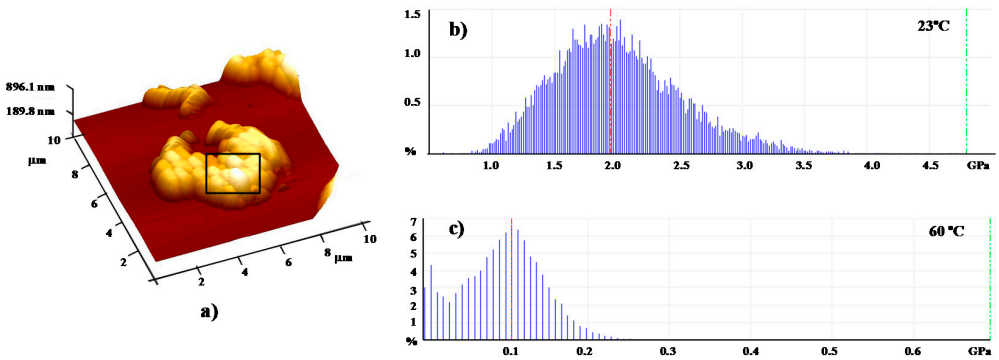

Figure 1. Results for PMMA:tetracosane (1:3): (**a**) 3D image tested; (**b**) Effective Young's modulus results at 23 °C; (**c**) Effective Young's modulus results at 60 °C.

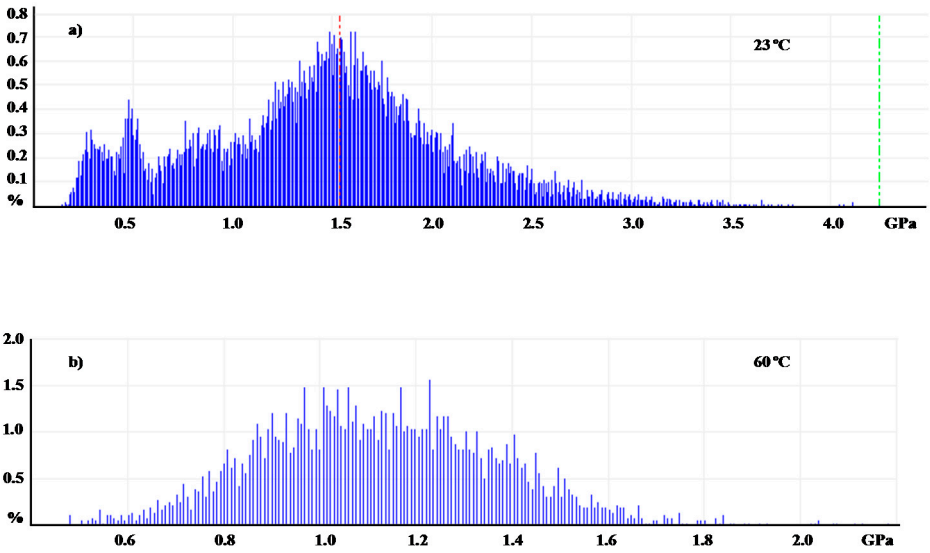

Figure 2. Results for PS:tetracosane (1:3): (**a**) Effective Young's modulus results at 23 °C; (**b**) Effective Young's modulus results at 60 °C.

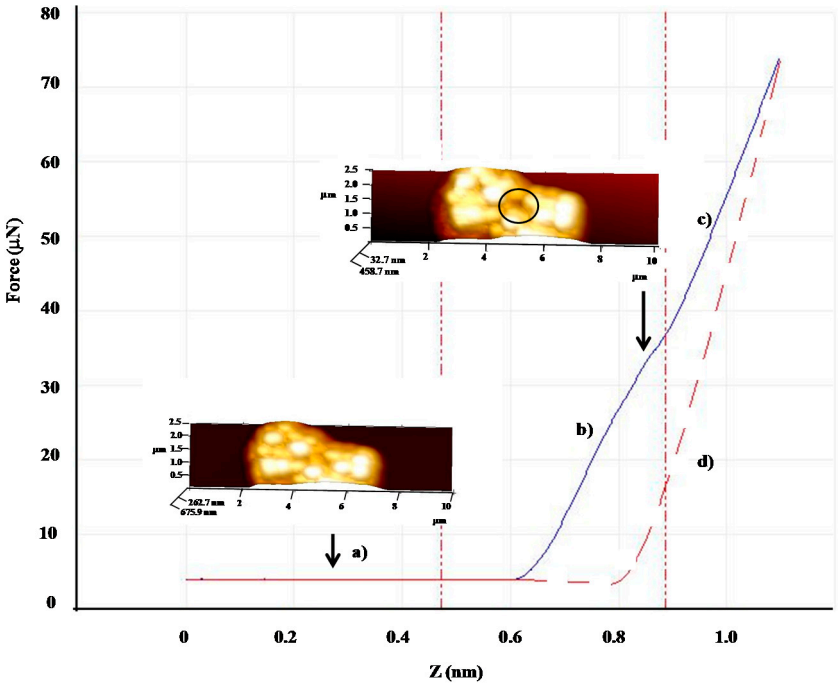

Figure 3. Mechanical testing of the elastic-plastic region by AFM of the MPCM composed by PMMA:tetracosane (1:3) microcapsule at 23 °C: (**a**) image of the sample before applying forces, no contact; (**b**) change in the slope, defined as the maximum force that can be applied to the sample ; (**c**) deformation of the sample; (**d**) retraction of the AFM probe until there is no contact between the tip and the sample.

The same test was performed at 60 °C, and the result was 11.4 µN, 63.5% less than that obtained at room temperature. The graphic representation is shown in Figure 4.

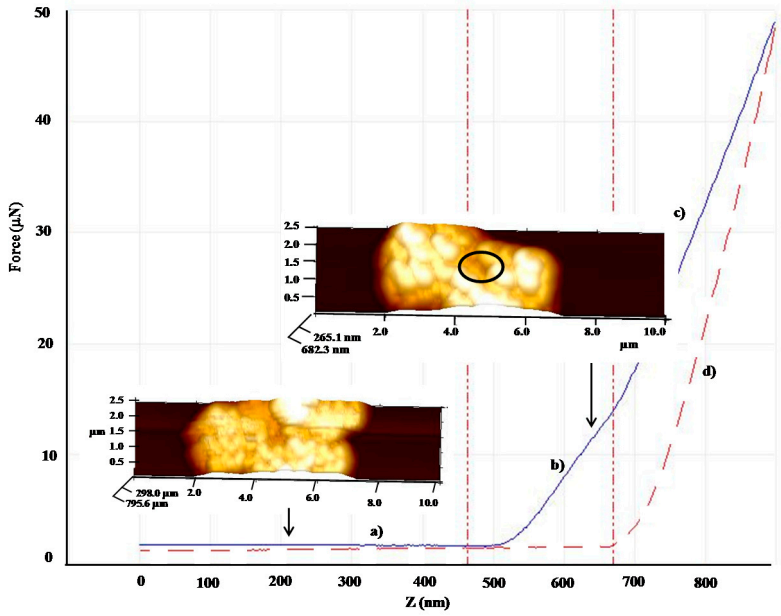

Figure 4. Mechanical testing of the elastic-plastic region by AFM of the MPCM composed by PMMA:tetracosane (1:3) microcapsule at 60 °C: (**a**) no contact, blue continuous line; (**b**) plastic penetration; (**c**) deformation of the sample; and (**d**) retraction of the AFM probe, red discontinuous line.

The same kind of test was done for the sample composed by PS and tetracosane at 23 °C and 60 °C. The results can be observed in Figures 5 and 6, respectively. At 23 °C, the maximum force applied to the top of the microcapsule before breaking it was 13.2 μN, while at 60 °C, this force was 5.3 μN. In the light of these results, the force value diminished 60% from room temperature to 60 °C.

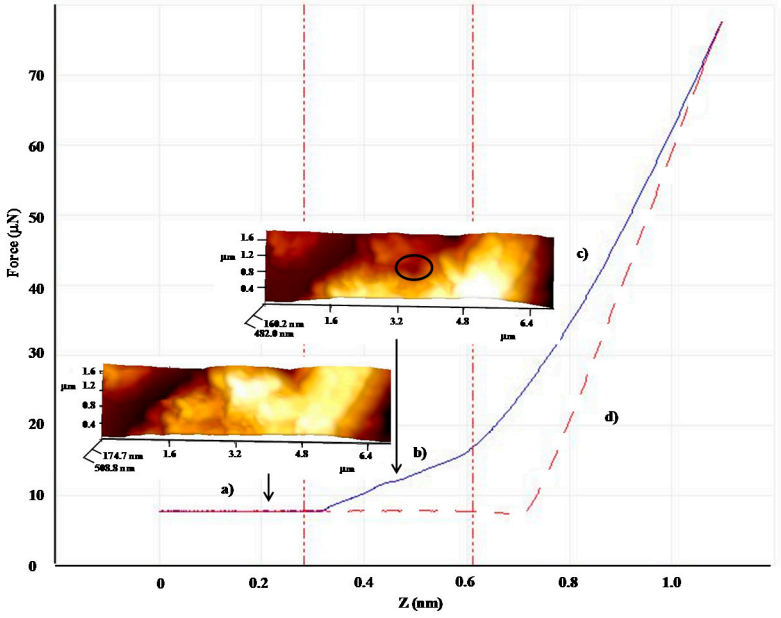

Figure 5. Mechanical testing of the elastic-plastic region by AFM of the MPCM composed by PS:tetracosane (1:3) microcapsule at 23 °C: (**a**) no contact, continuous line; (**b**) plastic penetration; (**c**) deformation of the sample; and (**d**) retraction of the AFM probe, discontinuous line.

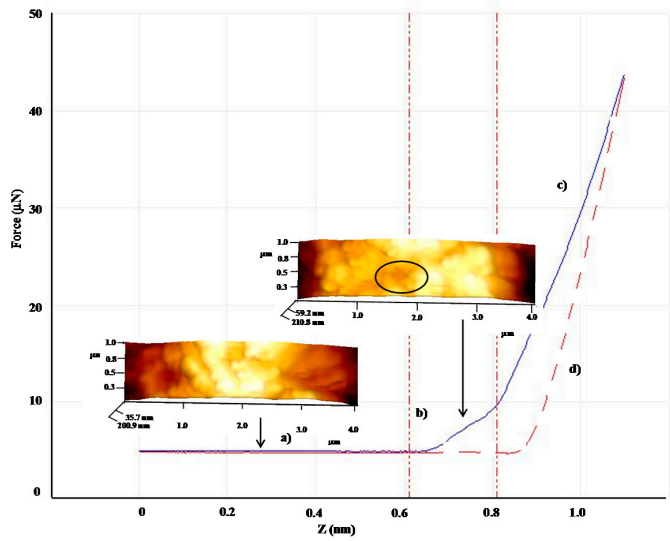

Figure 6. Mechanical testing of the elastic-plastic region by AFM of the MPCM composed by PS:tetracosane (1:3) microcapsule at 60 °C: (**a**) no contact, continuous line; (**b**) plastic penetration; (**c**) deformation of the sample; and (**d**) retraction of the AFM probe, discontinuous line.

Accordingly, for an encapsulation ratio of 1:3, PS has a better mechanical performance as a shell than PMMA, because the *E* value only decreases by 27% (as opposed to by 96% of PMMA) when increasing the temperature from 23 °C to 60 °C. However, no significant differences between using PS and PMMA shells were found in terms of the force needed to break the MPCMs with change in temperature from 23 °C to 60 °C (PS and PMMA displaying decrease of 60% and 64%, respectively).

Beyond the previous study comparing MPCM with different shells and same core, the mechanical response of two samples based on the encapsulation ratio was also evaluated. In this case, given the superior performance of PS, two samples using polystyrene (PS) as a shell and tetracosane as the core PCM, with encapsulation mass ratios of 1:3 (results shown above) and 1:1 were compared mechanically. This was performed using the same methodology and equipment as described for the previous measurements.

Histograms for the *E* results of PS and tetracosane with a mass ratio of 1:1 are shown in Figure 7. At 23 °C, a value of 0.9 GPa was obtained (Figure 7a), and at 60 °C this value decreased to 0.1 GPa (Figure 7b). A reduction in the *E* value by around 87% is achieved by increasing the temperature to 60 °C. Comparing this value reduction with the 1:3 MPCM encapsulation mass ratio, it can be seen that it is much better to use a ratio of 1:3, because the value only decreases by 27%.

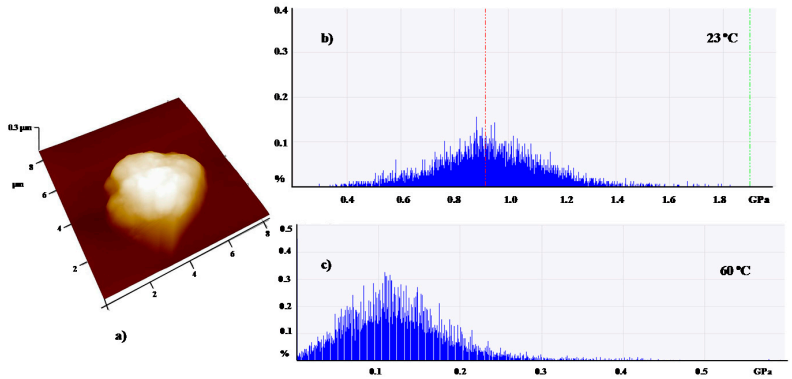

Figure 7. Results for PS and tetracosane for 1:1 encapsulation mass ratio: (**a**) 3D image tested; (**b**) Young's modulus results at 23 °C; (**c**) Young's modulus results at 60 °C.

To sum up, Table 1 shows a summary of the results, where it is important to highlight that, for the comparison study between encapsulation ratio 1:3 and 1:1 in PS:tetracosane, the higher *E* value takes place in the 1:3 encapsulation mass ratio. Hence, in terms of mechanical properties, the best combination core/sell/encapsulation mass ratio is PS/tetracosane/1:3. Moreover, the thermal properties for the 1:3 ratio are also better, as the PCM content increases.

Table 1. Summary of results for the different temperatures, different shells, and different encapsulation mass ratio by means AFM.

Shell:PCM Encapsulation Mass Ratio	PMMA:Tetracosane 1:3			PS:Tetracosane 1:3			PS:Tetracosane 1:1		
Temperature and % Reduction	23 °C	60 °C	Reduction (%)	23 °C	60 °C	Reduction (%)	23 °C	60 °C	Reduction (%)
E (GPa)	2.7	0.1	96	1.5	1.1	27	0.9	0.1	87
F (μN)	31.2	11.4	64	13.2	5.3	60	-	-	-

4. Conclusions

The comparison between samples containing tetracosane as the PCM, and PMMA or PS as the shell, shows that PS is a better option with an encapsulation mass ratio 1:3, due to the fact that the Effective Young's modulus value for PMMA decreases 3.5 times more than that of PS when increasing the temperature until the PCM is in liquid state. Additionally, the force required to break the MPCM system is approximately the same for both PS:tetracosane and PMMA/tetracosane at an encapsulation mass ratio of 1:3. The other study performed, which considered a comparison between PS:tetracosane systems with encapsulation mass ratios of 1:3 and 1:1, concluded that the Effective Young's Modulus in the 1:3 encapsulation mass ratio system was higher than that for 1:1; hence, its stiffness is higher. Therefore, to sum up, in terms of mechanical and thermal properties, the best combination core/sell/encapsulation mass ratio of the studies considering laboratory microcapsules is PS/tetrasosane/1:3.

Acknowledgments: The work was partially funded by the Spanish government (ENE2015-64117-C5-2R). The research leading to these results received funding from the European Union's Seventh Framework Program (FP7/2007–2013) under grant agreement No. PIRSES-GA-2013-610692 (INNOSTORAGE) and from the European Union's Horizon 2020 research and innovation program under grant agreement No. 657466 (INPATH-TES). The authors would like to thank the Catalan Government for the quality accreditation given to their research group DIOPMA (2014 SGR 1543).

Author Contributions: Jessica Giro-Paloma, Josep Maria Chimenos, and Ana Inés Fernández conceived and designed the experiments; Jessica Giro-Paloma performed the experiments and analyzed the data; Cemil Alkan contributed reagents and materials and prepared the samples; Jessica Giro-Paloma wrote the paper; Josep Maria Chimenos and Ana Inés Fernández reviewed the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Solé, A.; Martorell, I.; Cabeza, L.F. State of the art on gas—Solid thermochemical energy storage systems and reactors for building applications. *Renew. Sustain. Energy Rev.* **2015**, *47*, 386–398. [CrossRef]
2. Vandegaer, J.E. *Microencapsulation: Processes and Applications*; Springer Science & Business Media: Berlin, Germany, 2012.
3. Farid, M.M.; Khudhair, A.M.; Razack, S.A.K.; Al-Hallaj, S. A review on phase change energy storage: Materials and applications. *Energy Convers. Manag.* **2004**, *45*, 1597–1615. [CrossRef]
4. Konuklu, Y.; Ostry, M.; Paksoy, H.O.; Charvat, P. Review on Using Microencapsulated Phase Change Materials (PCM) in Building Applications. *Energy Build.* **2015**, *106*, 134–155. [CrossRef]
5. Giro-Paloma, J.; Martínez, M.; Cabeza, L.F.; Fernández, A.I. Types, methods, techniques, and applications for Microencapsulated Phase Change Materials (MPCM): A review. *Renew. Sustain. Energy Rev.* **2016**, *53*, 1059–1075. [CrossRef]
6. Sari, A.; Alkan, C.; Biçer, A.; Altuntaş, A.; Bilgin, C. Micro/nanoencapsulated n-nonadecane with poly(methyl methacrylate) shell for thermal energy storage. *Energy Convers. Manag.* **2014**, *86*, 614–621. [CrossRef]

7. Sari, A.; Alkan, C.; Bilgin, C. Micro/nano encapsulation of some paraffin eutectic mixtures with poly(methyl methacrylate) shell: Preparation, characterization and latent heat thermal energy storage properties. *Appl. Energy* **2014**, *136*, 217–227. [CrossRef]
8. Wang, Y.; Shi, H.; Xia, T.D.; Zhang, T.; Feng, H.X. Fabrication and performances of microencapsulated paraffin composites with polymethylmethacrylate shell based on ultraviolet irradiation-initiated. *Mater. Chem. Phys.* **2012**, *135*, 181–187. [CrossRef]
9. Giro-Paloma, J.; Konuklu, Y.; Fernández, A.I. Preparation and exhaustive characterization of paraffin or palmitic acid microcapsules as novel phase change material. *Sol. Energy* **2015**, *112*, 300–309. [CrossRef]
10. Sánchez-Silva, L.; Rodríguez, J.F.; Romero, A.; Borreguero, A.M.; Carmona, M.; Sánchez, P. Microencapsulation of PCMs with a styrene-methyl methacrylate copolymer shell by suspension-like polymerisation. *Chem. Eng. J.* **2010**, *157*, 216–222. [CrossRef]
11. Sari, A.; Alkan, C.; Altintaş, A. Preparation, characterization and latent heat thermal energy storage properties of micro-nanoencapsulated fatty acids by polystyrene shell. *Appl. Therm. Eng.* **2014**, *73*, 1158–1166. [CrossRef]
12. Sari, A.; Alkan, C.; Kahraman Döğüşcü, D.; Biçer, A. Micro/nano-encapsulated n-heptadecane with polystyrene shell for latent heat thermal energy storage. *Sol. Energy Mater. Sol. Cells* **2014**, *126*, 42–50. [CrossRef]
13. Sánchez, L.; Sánchez, P.; de Lucas, A.; Carmona, M.; Rodríguez, J.F. Microencapsulation of PCMs with a polystyrene shell. *Colloid Polym. Sci.* **2007**, *285*, 1377–1385. [CrossRef]
14. Yu, F.; Chen, Z.H.; Zeng, X.R. Preparation, characterization, and thermal properties of microPCMs containing n-dodecanol by using different types of styrene-maleic anhydride as emulsifier. *Colloid Polym. Sci.* **2009**, *287*, 549–560. [CrossRef]
15. Pisello, A.L.; D' Alessandro, A.; Fabiani, C.; Fiorelli, A.P.; Ubertini, F.; Cabeza, L.F.; Materazzi, A.L.; Cotana, F. Multifunctional Analysis of Innovative PCM-filled Concretes. *Energy Procedia* **2017**, *111*, 81–90. [CrossRef]
16. Bajāre, D.; Kazjonovs, J.; Korjakins, A.; Merijs-Meri, R. Development of Cement and Lime Based Plaster with Microencapsulated Phase Change Materials (PCM). In Proceedings of the 12th International Conference on Energy Storage, Lleida, Spain, 16–18 May 2012; pp. 1–7.
17. Rozanna, D.; Salmiah, A.; Chuah, T.G.; Medyan, R.; Thomas Choong, S.Y.; Sa'Ari, M. A study on thermal characteristics of phase change material (PCM) in gypsum board for building application. *J. Oil Palm Res.* **2005**, *17*, 41–46.
18. Benita, S. *Microencapsulation: Methods and Industrial Applications*; CRC Press: Boca Raton, FL, USA, 2006.
19. Wang, H.; Wang, J.P.; Wang, X.; Li, W.; Zhang, X. Preparation and Properties of Microencapsulated Phase Change Materials Containing Two-Phase Core Materials. *Ind. Eng. Chem. Res.* **2013**, *52*, 14706–14712. [CrossRef]
20. Ma, Y.; Sun, S.; Li, J.; Tang, G. Preparation and thermal reliabilities of microencapsulated phase change materials with binary cores and acrylate-based polymer shells. *Thermochim. Acta* **2014**, *588*, 38–46. [CrossRef]
21. Sari, A.; Alkan, C.; Özcan, A.N. Synthesis and characterization of micro/nano capsules of PMMA/capric-stearic acid eutectic mixture for low temperature-thermal energy storage in buildings. *Energy Build.* **2015**, *90*, 106–113. [CrossRef]
22. Fernández Lladó, J. *Análisis Del Comportamiento Al Fuego De Materiales De Construcción Con Adición De Pcmr*; Universitat Politècnica de Catalunya (UPC): Barcelona, Spain, 2012.
23. Borreguero, A.M.; Garrido, I.; Valverde, J.L.; Rodríguez, J.F.; Carmona, M. Thermal Characterization of Gypsum Composites by Using Differential Scanning Calorimetry. Introduction Thermal Energy Storage Materials. In Proceedings of the Energy and Environment Knowledge Week (E2KW) 2013, Toledo, Spain, 20–22 November 2013.
24. Eddhahak-Ouni, A.; Drissi, S.; Colin, J.; Neji, J.; Care, S. Experimental and multi-scale analysis of the thermal properties of Portland cement concretes embedded with microencapsulated Phase Change Materials (PCMs). *Appl. Therm. Eng.* **2014**, *64*, 32–39. [CrossRef]
25. Sari-Bey, S.; Fois, M.; Krupa, I.; Ibos, L.; Benyoucef, B.; Candau, Y. Thermal characterization of polymer matrix composites containing microencapsulated paraffin in solid or liquid state. *Energy Convers. Manag.* **2014**, *78*, 796–804. [CrossRef]
26. Franquet, E.; Gibout, S.; Tittelein, P.; Zalewski, L.; Dumas, J.P. Experimental and theoretical analysis of a cement mortar containing microencapsulated PCM. *Appl. Therm. Eng.* **2014**, *73*, 30–38. [CrossRef]

27. Delgado, M.; Lázaro, A.; Mazo, J.; Zalba, B. Review on phase change material emulsions and microencapsulated phase change material slurries: Materials, heat transfer studies and applications. *Renew. Sustain. Energy Rev.* **2012**, *16*, 253–273. [CrossRef]
28. Joulin, A.; Zalewski, L.; Lassue, S.; Naji, H. Experimental investigation of thermal characteristics of a mortar with or without a micro-encapsulated phase change material. *Appl. Therm. Eng.* **2014**, *66*, 171–180. [CrossRef]
29. Serrano, S.; Barreneche, C.; Rincón, L.; Boer, D.; Cabeza, L.F. Optimization of three new compositions of stabilized rammed earth incorporating PCM: Thermal properties characterization and LCA. *Constr. Build. Mater.* **2013**, *47*, 872–878. [CrossRef]
30. Serrano, S.; Barreneche, C.; Rincón, L.; Boer, D.; Cabeza, L.F. Stabilized rammed earth incorporating PCM: Optimization and improvement of thermal properties and Life Cycle Assessment. *Energy Procedia* **2012**, *30*, 461–470. [CrossRef]
31. Menoufi, K.; Castell, A.; Navarro, L.; Pérez, G.; Boer, D.; Cabeza, L.F. Evaluation of the environmental impact of experimental cubicles using Life Cycle Assessment: A highlight on the manufacturing phase. *Appl. Energy* **2012**, *92*, 534–544. [CrossRef]
32. Konuklu, Y. Microencapsulation of phase change material with poly(ethylacrylate) shell for thermal energy storage. *Int. J. Energy Res.* **2014**, *38*, 2019–2029. [CrossRef]
33. Konuklu, Y.; Paksoy, H.O.; Unal, M.; Konuklu, S. Microencapsulation of a fatty acid with Poly(melamine-urea-formaldehyde). *Energy Convers. Manag.* **2014**, *80*, 382–390. [CrossRef]
34. Konuklu, Y.; Unal, M.; Paksoy, H.O. Microencapsulation of caprylic acid with different wall materials as phase change material for thermal energy storage. *Sol. Energy Mater. Sol. Cells* **2014**, *120*, 536–542. [CrossRef]
35. Giro-Paloma, J.; Barreneche, C.; Martínez, M.; Šumiga, B.; Fernández, A.I.; Cabeza, L.F. Mechanical response evaluation of microcapsules from different slurries. *Renew. Energy* **2016**, *85*, 732–739. [CrossRef]
36. Giro-Paloma, J.; Oncins, G.; Barreneche, C.; Martínez, M.; Fernández, A.I.; Cabeza, L.F. Physico-chemical and mechanical properties of microencapsulated phase change material. *Appl. Energy* **2013**, *109*, 441–448. [CrossRef]